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Synthesis, stereochemistry, and reactions of 2,5-diphenylsilacyclopentenes

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Abstract

1,1-Disubstituted derivatives of 2,5-diphenylsilacyclopent-3-enes, namely those having the 1,1-diphenyl, 1,1-dimethyl, 1-alkoxy-1-methyl and 1,1-dialkoxy, were prepared by a one-pot reaction of (1*E*, 3*E*)-1,4-diphenyl-1,3-butadiene and dichlorosilanes in the presence of magnesium. Each silacyclopentene was formed as a mixture of one trans and two cis isomers. 1-Ethoxy-1-methyl-2,5-diphenylsilacyclopent-3-ene and 1,1-diethoxy-2,5-diphenylsilacyclopent-3-ene were reacted with optically active alcohols to furnish the corresponding diastereomers. The absolute configuration of one of these diastereomers was determined by X-ray structure analysis. The mixture of cis and trans diastereomers was lithiated by lithium diisopropylamide (LDA) to obtain the trans forms selectively, with the stereoselectivity being determined by NOE experiments.

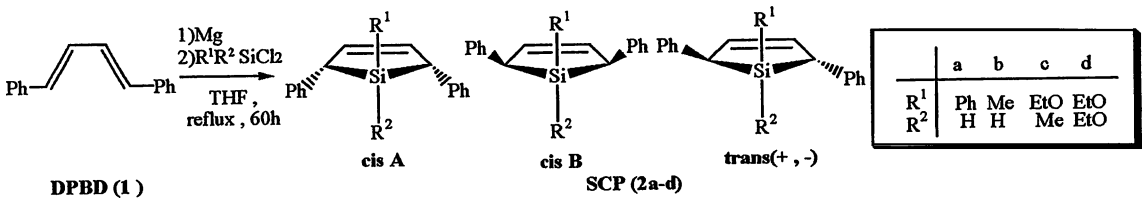
Introduction

The reactions and stereochemistry of silacyclopentenes having 2,5-disubstituents and a reactive 1-substituent are of interest in organic synthesis because a large and special steric effect through the reactive silicon atom is expected. Recently 2,5-disubstituted or 2-substituted silacyclopentenes were prepared in good yields from siloles or diallylsilanes [1, 2]. The silylation of dienes with dichlorosilanes in the presence of magnesium is the most straightforward method to prepare 2,5-disubstituted silacyclopentenes. Metallic magnesium is known to react with (1*E*, 3*E*)-1,4-diphenylbuta-1,3-diene in THF to yield the halide-free organomagnesium compound, 1,4-diphenyl-2-butene-1,4-diylmagnesium [3]. However, the reaction of magnesium with 1,3-butadiene or isoprene is usually accompanied by dimerization, trimerization and oligomerization [4]. Although the utilization of these organomagnesium compounds has been limited, several silacyclopentenes have recently been prepared by reacting 1,3-butadienes with dichlorosilanes using magnesium [5–7]. Substituted (2-butene-1,4-diyl)magnesium complexes are conveniently prepared through the reaction of activated magnesium with the corresponding 1,3-dienes. Thus, dichlorodimethylsilane reacts with (1,4-diphenyl-2-butene-1,4-diyl)magnesium to give the cis-1,1-dimethyl-2,5-diphenylsilacyclopent-3-ene [3, 8]. Although the structure of the magnesium complex has been determined [9], the reaction of dialkoxydichlorosilanes with the complex has not been reported.

We previously reported the synthesis of the 1-substituted derivatives of 2,5-diphenylsilacyclopent-3-enes by a one-pot reaction of magnesium with (1*E*, 3*E*)-1,4-diphenyl-1,3-butadiene (DPBD) (**1**) and various chlorosilanes [10–12]. In this paper, the preparation, stereochemistry, and reactions of the 2,5-diphenylsilacyclopent-3-enes (SCP) (**2a–d**) (Schemes 1 and 2) and their corresponding optically active alkoxy diastereomers (Schemes 3 and 4) were investigated using both X-ray structure analysis and NOE experiments.

Results and discussion

Preparation of 1,1-disubstituted derivatives of 2,5-diphenylsilacyclopent-3-enes was investigated. To a



Scheme 1.

mixture of magnesium (Grignard reaction grade) and (1*E*, 3*E*)-1,4-diphenyl-1,3-butadiene in THF were added dichlorosilanes at room temperature. The mixture was stirred at 25–67 °C for 40–65 h. The 2,5-diphenylsilacyclopent-3-enes (**2a–d**) were obtained by distillation (Scheme 1) as a mixture of cis and trans isomers (Table 1). The trans isomers, including the racemic forms, and the cis isomers including the meso forms, were assigned by 2D-NMR. The H-H COSY 2D NMR spectrum (Figure 1) shows the existence of the cis and trans isomers, and their accompanying ratios in each 2,5-diphenylsilacyclopent-3-ene (**2a–d**) were confirmed by ^{1}H-NMR.

Figure 1 shows the H-H COSY NMR spectrum of the 1,1-diethoxy-2,5-diphenylsilacyclopent-3-enes (**2d**). The cross peaks (f, e), (b, a) and (f′, e′) indicate the spin couplings of the ethoxy groups, of the CH_2 and the CH_3 groups, respectively. These three cross peaks reflect the existence of three different chemical environments for the ethoxy groups. The cross peak (f, e) shows the spin coupling of the peaks f and e of the ethoxy groups, which are affected by the two phenyl groups and are consequently shifted the farthest upfield. The cross peak (f′, e′) shows the spin coupling of the peaks f′ and e′ of the ethoxy groups which are not affected by phenyl groups. Therefore, the cross peaks (f, e) and (f′, e′) are assigned to the ethoxy groups of the cis isomers. Finally the cross peak (b, a) shows the spin coupling of peaks f and e of the ethoxy groups which are affected by one phenyl group. Therefore, the cross peak (b, a) is located between cross peaks (f, e) and (f′, e′), respectively, and is assigned to the ethoxy groups of the trans isomers. Considering the above factors, Figure 1 lends strong evidence to the existence of the cis and trans isomers of 1,1-diethoxy-2,5-diphenylsilacyclopent-3-enes (**2d**).

Isolation of trans-1,1-disubstituted derivatives of 2,5-diphenylsilacyclo-pent-3-enes was investigated. For optical resolution, the separation of the racemic compounds from the meso compounds is essential. To separate the trans isomers, including the racemic compounds, from the cis isomers, including the meso compounds, the 2,5-diphenylsilacyclopentenes **2c,d** were lithiated by lithium diisopropylamide (LDA) in THF at −78 °C for 10 h, then reacted with alkyl bromides to alkylate at the 2-position of the cis isomers **2c,d**. The alkyl substituted products **4c,d** were separated from the trans 2,5-diphenylsilacyclopentenes **5c,d** by column chromatography (eluent: hexane) (Scheme 2). Table 2 shows the yields and isomer ratios. The selective alkylation of the cis form can be explained by the different steric effects of the cis and trans forms, which can be estimated by DIFNOE spectra. Figure 2 shows the DIFNOE spectra of the 1,1-diethoxy-2,5-diphenylsilacyclopent-3-enes (**2d**); the lower spectrum is the ^{1}H-NMR spectrum and the upper spectrum is the DIFNOE spectrum. In Figure 2, only the trans

Table 1. Preparations of silacyclopentenes **2a–d**[a].

Compounds	Time (h)	Temp (°C)	Yield (%)[b]	Isomer ratio[c] (*trans*: *cis*A + *cis*B)
2a	40	67	24	35:65
2b	40	67	22	24:76
2c	65	67	71	26:74
2d	65	67	84	58:42

[a]Molar ratio; (DPBD) (**1**): $R^1R^2SiCl_2$: Mg = 0.05:0.06:0.06.
[b]Isolated yields by distillation; b.p. (°C/mmHg, 1 mmHg = 133.322 Pa): **2a** 190.0–193.5/2.0, **2b** 135.0–137.5/4.0, **2c** 155.0–158.0/1.0, **2d** 144.0–146.0/2.0. The products were fully characterized by ^{1}H-NMR, ^{13}C-NMR, IR and mass spectra.
[c]Isomer ratios were determined by ^{1}H-NMR analysis of products.

Table 2. Yield of silacyclopentenes **4c**, **4d**, **5c** and **5d**.

Compounds	Temp (°C)	Time (h)	Yield (%)[a]
4c	−78	8 and 3	16
4d	−78	8 and 3	41
5c	−78	8 and 3	41
5d	−78	8 and 3	46

[a]Isolated yields by column chromatography (eluent: hexane).

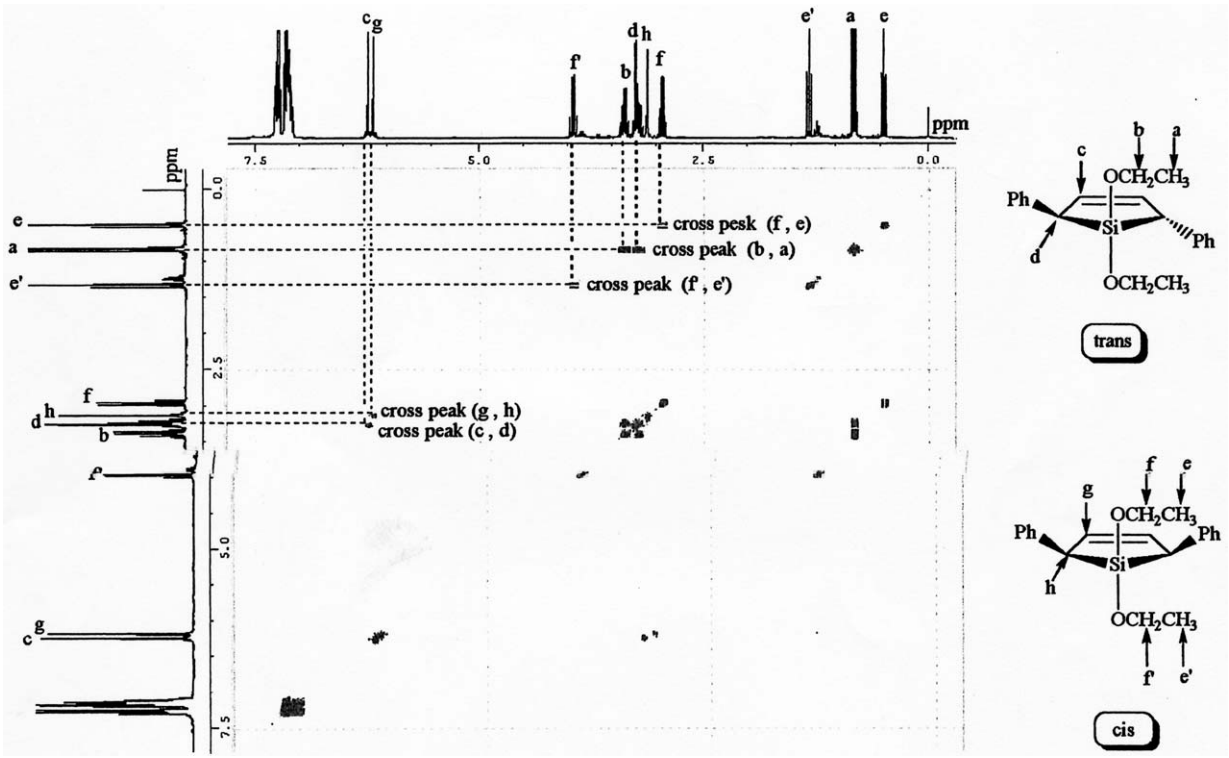
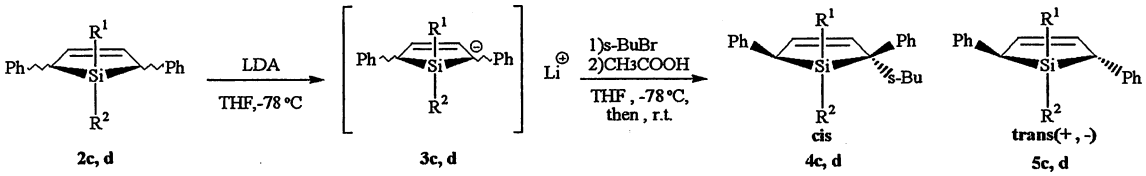


Figure 1. H-H COSY NMR spectrum of **2d** in $CDCl_3$ (500 MHz).



Scheme 2.

isomer shows an enhancement peak of the olefin proton (enhancement 'A') and the methine proton (enhancement 'B'). These results indicate that the phenyl groups of the trans forms are closer to the silacyclopentene ring than those of the cis form. Therefore, the cis forms have more space to react with the alkyl bromides.

Synthesis of diastereomeric 1,1-disubstituted derivatives of 2,5-diphenyl-silacyclopent-3-enes was performed. The reaction of **2c,d** with optically active alcohols in toluene at 110 °C for 10 h in the presence of *p*-toluenesulfonic acid gave the corresponding diastereomers (**6c**, **6′c**, **6d** and **6′d**) (Scheme 3). Their yields and isomer ratios are shown in Table 3. The isomer ratio was not changed in this reaction. In the two cis isomers of the borneoxy derivatives (cis A and cis B), cis A, 1-(*l*-borneoxy)-1-methyl silacyclopentene (**6′c**) crystallized from the mixture of the other isomers and the structure of 1-*l*-borneoxy-1-methylsilacyclopentene (**6′c**) was determined by single

Table 3. Yield and isomer ratio of **6c,d** and **6′c,d**.

R*O	R^2	Products	Temp (°C)	Time (h)	Yield (%)[a]	Isomer ratio/ *trans:cis*
l-Menthoxy	Me	**6c**	110	10	75	26:74
l-Menthoxy	–	**6d**	110	10	77	58:42
l-Borneoxy	Me	**6′c**	110	10	70	26:74
l-Borneoxy	–	**6′d**	110	10	76	58:42

[a]Isolated yields by column chromatography (eluent: hexane).
[b]Isomer ratios were determined by ^{1}H-NMR analysis of products.

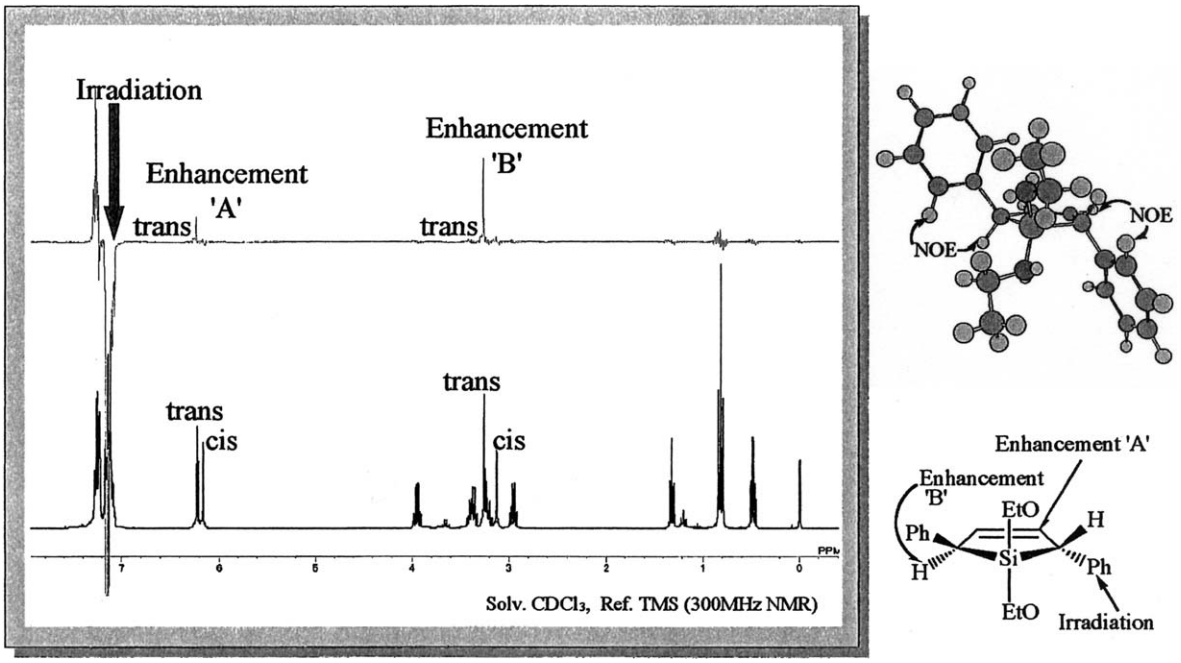
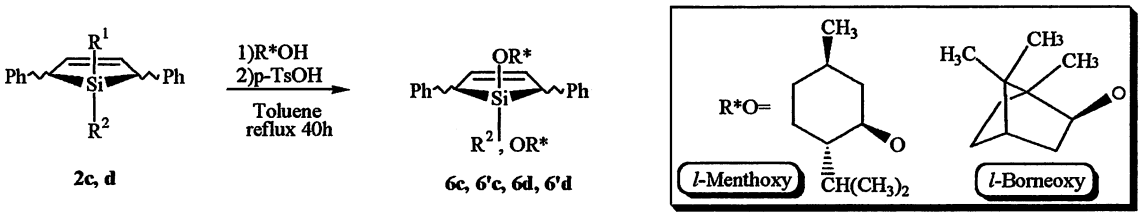


Figure 2. DIFNOE spectra of **2d** in $CDCl_3$.



Scheme 3.

crystal X-ray diffraction methods. The structural diagram is shown in Figure 3. This easy crystallization suggests that cis A of the 1-*l*-borneoxy-1-methyl silacyclopentene (**6′c**) has the most stable structure.

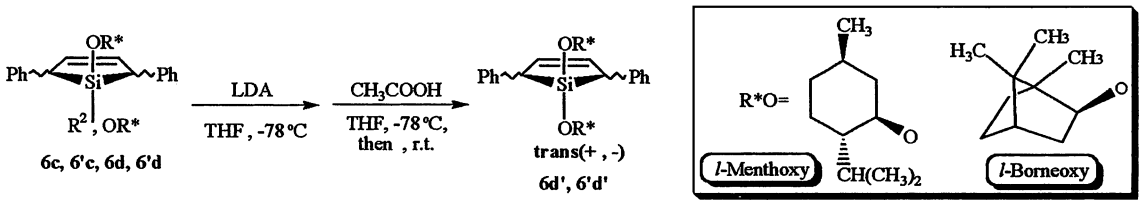
Stereoselective isomerization of 1,1-disubstituted derivatives of 2,5-di-phenylsilacyclopent-3-enes was performed. The disubstituted 2,5-diphenylsilacyclopentenes **6d** and **6′d** were lithiated with LDA to change the isomer ratio of the cis and trans compounds. Compounds **6d** and **6′d** were lithiated at the 2 position of the silacyclopentene ring in THF at −78 °C for 10 h, then reacted with acetic acid (Scheme 4). The yields and isomer ratios are shown in Table 4. In Figure 4 the change of the NMR peaks of the isomers in the reaction is shown.

The resulting bis(*l*-menthoxy)SCP compound **6d′** was almost entirely the trans isomer while the resulting bis(*l*-borneoxy)SCP **6′d′** was only the trans isomer. This isomerization can be explained by the difference in the steric interactions of the substituents on the cis and trans isomers. In the cis isomers, the two phenyl rings interact with the same large alkoxy group, which is energetically quite unfavourable due to a severe steric effect (a buttressing effect), while in the trans isomers each phenyl ring interacts with only one large alkoxy group and can move slightly away from this interaction

Table 4. Yield and isomer ratio of **6d′** and **6′d′**.

R*O	Compound	Temp (°C)	Time (h)	Yield (%)	Isomer ratio/ *trans:cis*
l-Menthoxy	**6d′**	−78	8 and 3	52	90:10
l-Borneoxy	**6′d′**	−78	8 and 3	51	Only trans

[a]Isolated yields by column chromatography (eluent: hexane).
[b]Isomer ratios were determined by ^{1}H-NMR analysis of products.



Scheme 4.

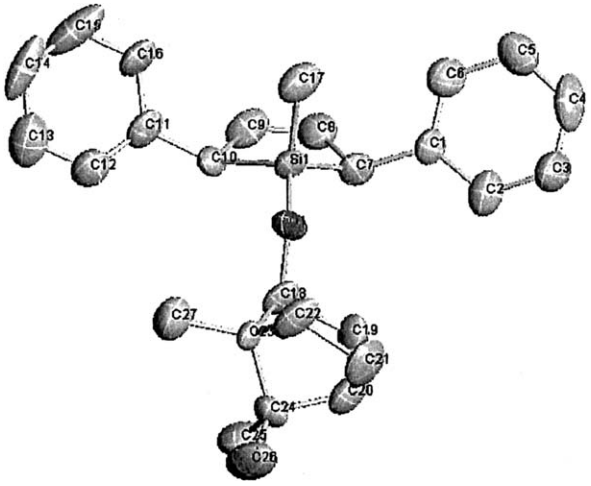


Figure 3. Diagram of the *l*-borneoxy, methyl silacyclopentene (**6′c**) with atoms represented by thermal ellipsoids. Hydrogen atoms have been omitted for clarity.

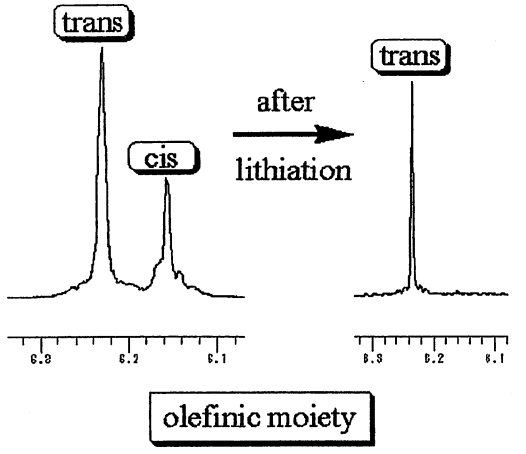


Figure 4. Change of NMR peaks by lithiation of **6′d**.

(and towards the cyclopentene ring). Indeed, the DIFNOE spectra (Figure 5) show a larger interaction of the phenyl rings with the silacyclopentene in the trans isomers than in the cis, thereby lending evidence to the fact that the phenyl rings have moved away from the steric interaction with the large alkoxy groups in the trans isomers, but cannot do so in the cis isomers. Thus the deprotonation–reprotonation sequence allows one to isomerize the less stable cis isomers completely or nearly completely to the more stable trans isomers.

Conclusions

We have shown that several 1,1-disubstituted 2,5-diphenylsilacyclopent-3-enes **2a–d** can be easily prepared and the trans and cis isomers separated. The 1-alkoxy and 1,1-dialkoxy derivatives **2c,d** can be deprotonated to give a mixture of the cis alkylated products **4c,d** and the unalkylated trans isomers **5c,d**. Finally the 1,1-dialkoxy derivatives prepared from **2c,d** and optically active alcohols, menthol and borneol, can be prepared and deprotonated to give larger amounts of the trans isomers. An X-ray crystal structure of the mono-*l*-borneoxy SCP has been solved. Further experiments in this area are underway.

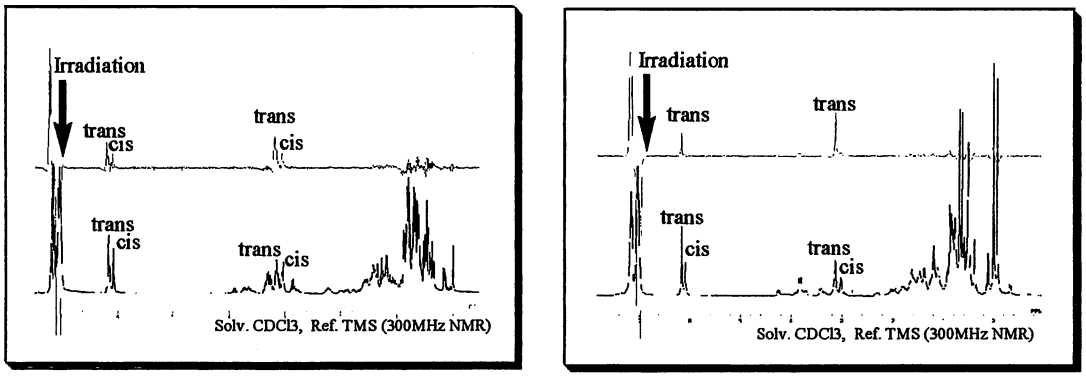
Experimental

General

All reactions were performed under an inert nitrogen atmosphere. Air-sensitive reagents were transferred in an argon-filled glove box. THF and toluene were freshly distilled under nitrogen from sodium immediately prior to use. Hexane was stirred over sulfuric acid, distilled from calcium hydrate, and stored over 4 Å molecular sieves. NMR spectra were obtained on a JEOL ECP-500 (500 MHz) spectrometer in $CDCl_3$ solutions. All of the chemical shifts are reported in ppm (δ) downfield from internal tetramethylsilane. Elemental analyses were performed at the Instrument Center of the Science University of Tokyo.

*Preparation of 2,5-diphenylsilacyclopent-3-enes (**2a–d**)*

General procedure: In most examples, dichlorosilanes (3.83 mmol) in THF were added to (1*E*, 3*E*)-1,4-



6d **6'd**

Figure 5. DIFNOE spectrum of **6d**, **6'd**.

diphenylbuta-1,3-diene (3.83 mmol) and magnesium (for Grignard reactions 3.83 mmol) in THF (60 mL) at room temperature. The mixture was stirred at 25–67 °C for 40–65 h. After evaporation of THF from the reaction mixture, the residue was removed by filtration. The filtrate was evaporated in order to remove the solvent, and the residue was distilled under reduced pressure to give **2a**–**d**.

1-Phenyl-2,5-diphenylsilacyclopent-3-ene (**2a**): Compound **2a** was obtained in 24% isolated yield by a reaction at 67 °C for 40 h; ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 7.65–6.86 (m, aromatic H, 15H), 6.38 (s, = CH for cis B, 2H), 6.35 (l) (s, = CH for trans, 1H), 6.30 (s, = CH trans, 1H), 6.18 (s, = CH for cis A, 2H), 4.99 (e) (s, Si-H for cis B, 1H), 4.52 (s, Si-H for trans, 1H), 4.22 (s, Si-H for cis A, 1H), 3.73 (s, CH for trans, 2H), 3.70 (s, CH for cis B, 2H), 3.58 (s, CH for trans, 2H), 3.54 (s, CH for cis A, 2H) ^{13}C-NMR δ for each pair of cis and trans isomers: (139.1, 138.7), (135.4, 134.9), (129.7, 128.6, 128.5), (128.2, 128.0), (127.7, 127.2, 127.0), (124.8, 124.4), (40.0, 39.5), and (32.6, 32.3, 31.9); MS *m/z* 312 (M^+); Anal. calculated for $C_{22}H_{20}Si$: C, 84.6%; H, 6.5%. Found: C, 84.4%; H, 6.6%.

1-Methyl-2,5-diphenylsilacyclopent-3-ene (**2b**): Yield 22% in a reaction at 67 °C for 40 h; ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 7.10–7.26 (m, aromatic H, 10H), 6.19 (s, = CH for trans, 2H), 6.15 (s, = CH for cis B, 2H), 6.08 (s, = CH for cis A, 2H), 4.52 (s, Si-H for cis B, 1H), 4.06 (s, Si-H for trans, 1H), 3.70 (j) (s, Si-H for cis A, 1H), 3.61 (s, CH for trans, 1H), 3.55 (s, CH for cis B, 2H), 3.31 (s, CH for trans, 1H), 3.25 (s, CH for cis A, 2H), 0.47 (s, CH_3 for cis A, 3H), −0.08 (s, CH_3 for trans, 3H), −0.60 (s, CH_3 for cis B, 3H); ^{13}C-NMR δ for each pair of cis and trans isomers: (137.8, 137.6), (129.1, 128.9), (128.4, 128.3), 125.5, 125.3, (17.9, 17.7, 17.2), and (−9.2, −10.7, −11.9,); MS *m/z* 250 (M^+).

1-Ethoxy-1-methyl-2,5-diphenylsilacyclopent-3-ene (**2c**): Yield 71% in a reaction at 67 °C for 65 h; ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 7.27–7.07 (m, aromatic H, 10H), 6.24 (s, = CH for trans, 2H), 6.20 (s, = CH for cis B, 2H), 6.15 (s, = CH for cis A, 2H), 3.42 and 3.26 (s, CH for trans, 2H), 3.35 (s, CH for cis A, 2H), 3.08 (s, CH for cis B, 2H), 3.88 (q, CH_2 for cis A, J = 6.9 Hz, 2H), 3.26 (q, CH_2 for trans, J = 6.9 Hz, 2H), 2.84 (q, CH_2 for cis B, J = 6.9 Hz, 2H), 1.30 (t, CH_2 for cis A, J = 6.9 Hz, 3H), 0.82 (t, CH_2 for trans, J = 6.9 Hz, 3H), 0.40 (t, CH_2 for cis B, J = 6.9 Hz, 3H), 0.49 (s, Si–CH_2 for cis B, J = 6.9 Hz, 3H), 0.03 (s, Si–CH_2 for trans, J = 6.9 Hz, 3H), −0.48 (s, Si–CH_2 for cis A, J = 6.9 Hz, 3H); ^{13}C-NMR δ for each pair of cis and trans isomers: (142.9, 142.8, 142.0, 142.7), (135.5, 135.4, 134.7), (128.7, 128.6), (127.2, 127.0, 126.9), (124.8), (59.5), (39.6, 38.6, 37.8, 37.3), (18.7, 18.0, 17.4), and (−3.1, −5.0, −7.4); MS *m/z* 294 (M^+).

1,1-Diethoxy-2,5-diphenylsilacyclopent-3-ene (**2d**): Yield 84% in a reaction at 67 °C for 65 h; ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 7.10–7.26 (m, aromatic H, 10H), 6.23 (s, = CH for trans 2H), 6.17 (s, = CH for cis 2H), 3.95 (q, CH_2 for cis, J = 6.9 Hz, 2H), 3.38 (q, CH_2 for trans, J = 6.9 Hz, 2H), 3.26 (q, CH_2 for trans, J = 6.9 Hz, 2H), 3.96 (q, CH_2 for cis, J = 6.9 Hz, 2H), 3.26 (s, CH for trans, 2H), 3.13 (s, CH for cis, 2H), 1.32 (t, CH_2 for cis, J = 6.9 Hz, 3H), 0.82 (t, 2 × CH_2 for trans, J = 6.9 Hz, 6H), 0.48 (t, CH_2 for cis, J = 6.9 Hz, 3H); ^{13}C-NMR δ for each pair of cis and trans isomers: (141.5, 141.3), (135.1, 134.3), (128.4, 128.2), (127.3, 127.2), 124.7, (59.4, 59.1,

59.0), (35.5, 35.1), and (18.4, 17.7, 17.4); MS *m/z* 324 (M^+); Analyzed and calculated for $C_{20}H_{24}O_2Si$: C, 74.0%; H, 7.5%. Found: C, 74.4%; H, 7.4%.

Isolation of the trans 1,1-disubstituted derivatives of 2,5-diphenylsilacyclopent-3-enes, ***4c, 4d, 5c,*** *and* ***5d***

General procedure: Compounds **2c,d** were lithiated by lithium diisopropylamide (LDA) in THF at 78 °C for 10 h, then reacted with alkyl bromides to substitute the 2-position of cis-**2c,d** to alkyl and alkyl substituted products **4c,d** which were separated from trans-**5c,d** by column chromatography (eluent: hexane).

1-Ethoxy-1-methyl-2-sec-butyl-2,5-diphenylsilacyclopent-3-ene (**4c**): Compound **4c** was obtained in 16% isolated yield by a reaction at –78 °C; ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 7.27–7.07 (m, aromatic H, 10H), 6.15 (s, = CH, 2H), 3.35 (s, CH, 1H), 3.88 (q, CH_2, J = 6.9 Hz, 2H), 2.22–2.38 (m, CH, 1H), 1.83–1.92 (m, CH_2 J = 6.9 Hz, 2H), 1.26–1.32 (m, CH_2 J = 6.9 Hz, 2H), 1.30 (t, CH_2 for cis A, J = 6.9 Hz, 3H), 0.98 (t, CH_2 J = 6.9 Hz, 3H), 0.78 (t, CH_3 J = 6.9 Hz, 3H), 1.31 (d, CH_2, J = 6.9 Hz, 3H), 0.68 (d, CH_2, J = 6.9 Hz, 3H), −0.48 (s, Si–CH_2, J = 6.9 Hz, 3H); ^{13}C-NMR δ-142.9, 142.7, 135.5, 134.7, 128.7, 127.2, 126.9, 124.8, 59.5, 39.6, 38.6, 37.8, 37.3, 28.5, 22.2, 18.3, 17.9, 18.0, 17.4, −3.1, and −7.4; MS *m/z* 350 (M^+); Analyzed and calculated for $C_{23}H_{30}OSi$: C, 78.8%; H, 8.6%. Found: C, 78.5%; H, 8.2%.

1,1-Diethoxy-2-sec-butyl-2,5-diphenylsilacyclopent-3-ene (**4d**): Yield 41% in a reaction at −78 °C; ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 7.27–7.07 (m, aromatic H, 10H), 6.17 (s, = CH, 2H), 3.95 (q, CH_2, J = 6.9 Hz, 2H), 3.96 (q, CH_2, J = 6.9 Hz, 2H), 3.14 (s, CH, 1H), 2.66 (q, CH_2 J = 6.9 Hz, 2H), 2.22–2.38 (m, CH, 1H), 1.83–1.92 (m, CH_2, J = 6.9 Hz, 2H), 1.26–1.32 (m, CH_2, J = 6.9 Hz, 2H), 1.32 (t, CH_2, J = 6.9 Hz, 3H), 0.98 (t, CH_2, J = 6.9 Hz, 3H), 0.78 (t, CH_2, J = 6.9 Hz, 3H), 1.31 (d, CH_2, J = 6.9 Hz, 3H), 0.68 (d, CH_2, J = 6.9 Hz, 3H), 0.48 (t, CH_2, J = 6.9 Hz, 3H); ^{13}C-NMR δ: 141.3, 135.1, 128.4, 127.3, 124.7, 59.0, 28.5, 20.7, 18.3, 17.9, 35.1, and 18.4; MS *m/z* 380 (M^+); Analyzed and calculated for $C_{24}H_{32}O_2Si$: C, 75.7%; H, 8.5%. Found: C, 75.2%; H, 8.4%.

trans-1-Ethoxy-1-methyl-2,5-diphenylsilacyclopent-3-ene (**5c**): Yield 41% in a reaction at −78 °C; ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 7.27–7.07 (m, aromatic H, 10H), 6.24 (s, = CH, 2H), 3.42 and 3.26 (s, CH, 2H), 3.26 (q, CH_2, J = 6.9 Hz, 2H), 0.82 (t, CH_2, J = 6.9 Hz, 3H), 0.03 (s, Si–CH_2, J = 6.9 Hz, 3H); ^{13}C-NMR δ: 142.9, 142.7, 134.7, 128.6, 127.0, 124.8. 59.5, 38.6, 18.7, and −5.0; MS *m/z* 294 (M^+).

trans-1,1-Diethoxy-1-methyl-2,5-diphenylsilacyclopent-3-ene (**5d**): Yield 46% in a reaction at −78 °C; ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 7.10–7.26 (m, aromatic H, 10H), 6.23 (s, = CH, 2H), 3.38 (q, CH_2, J = 6.9 Hz, 2H), 3.26 (q, CH_2, J = 6.9 Hz, 2H), 3.26 (s, CH, 2H), 0.82 (t, 2 × CH_2, J = 6.9 Hz, 6H); ^{13}C-NMR δ:41.3, 135.1, 128.2, 127.2, 124.7, 59.1, 35.5, and 17.4; MS *m/z* 324 (M^+); Anal. calcd. for $C_{20}H_{24}O_2Si$: C, 74.0%; H, 7.5%. Found: C, 74.4%; H, 7.4%.

*Preparation of 2,5-diphenylsilacyclopent-3-enes (***6c***,* **6d***,* **6′c***, and* **6′d***) from* **2c** *or* **2d**

General procedure: A solution of **2c/2d** (9.26 mmol), *l*-menthol (37.0 mmol) and *p*-toluenesulfonic acid (0.0278 mmol) in toluene (5 mL) was refluxed for 10 h. The resulting solution was evaporated to remove toluene, and the residue was distilled under reduced pressure to give **6c/6d**. The reaction of **2c/2d** with *l*-borneol gave **6′c/6′d** by a similar method.

1-*l*-Menthoxy-1-methyl-2,5-diphenylsilacyclopent-3-ene (**6c**): Compound **6c** was obtained in 75% isolated yield by a reaction at 110 °C for 10 h; ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 7.27–7.07 (m, aromatic H, 10H), 6.24 (s, = CH for trans, 2H), 6.20 (s, = CH for cis B, 2H), 6.15 (s, = CH for cis A, 2H), 3.42 and 3.26 (s, CH for trans, 2H), 3.35 (s, CH for cis A, 2H), 3.08 (s, CH for cis B, 2H), 3.37–3.42 (m, OCH, 1H), 3.30–3.37 (m, OCH, 1H), 2.30–2.39 (m, CH, 1H), 2.02–2.20 (m, CH, 1H), 0.22–0.17 (m, CH, CH_2, and CH_2, 17H), 0.49 (s, Si–CH_2 for cis B, J = 6.9 Hz, 3H), 0.03 (s, Si–CH_2 for the trans isomer, J = 6.9 Hz, 3H), −0.48 (s, Si–CH_2 for cis A, J = 6.9 Hz, 3H); ^{13}C-NMR δ for each pair of cis and trans isomers: (142.9, 142.8, 142.0, 142.7), (135.5, 135.4, 134.7), (128.7, 128.6), (127.2, 127.0, 126.9), (124.8), 73.7, 59.5, 49.9, 45.7, (39.6, 38.6, 37.8, 37.3), 34.4, 31.6, 25.5, 23.0, 22.6, 21.1, and 16.2; MS *m/z* 404 (M^+); Anal. Calcd. for $C_{27}H_{36}OSi$: C, 80.1%; H, 9.0%. Found: C, 80.2.4%; H, 8.9%.

1-*l*-Borneoxy-1-methyl-2,5-diphenylsilacyclopent-3-ene (**6′c**): Yield 70% in a reaction at 110 °C for 10 h; ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 7.27–7.07 (m, aromatic H, 10H), 6.24 (s, = CH for trans, 2H), 6.20 (s, = CH for cis B, 2H), 6.15 (s, = CH for cis A, 2H), 4.25–4.37 (d, OCH J = 6.9 Hz, 1H), 3.88–3.96 (d, OCH J = 6.9 Hz, 1H), 3.42 and 3.26 (s, CH for trans, 2H), 3.35 (s, CH for cis A, 2H), 3.08 (s, CH for cis B, 2H), 2.28–0.18 (m, CH, CH_2, and CH_2, 17H), 0.49 (s, Si–CH_2 for cis B, J = 6.9 Hz, 3H), 0.03 (s, Si–CH_2 for the trans isomer, J = 6.9 Hz, 3H), −0.48 (s, Si–CH_2 for cis A, J = 6.9 Hz, 3H); ^{13}C-NMR δ for each pair

of cis and trans isomers: (142.9, 142.8, 142.0, 142.7), (135.5, 135.4, 134.7), (128.7, 128.6), (127.2, 127.0, 126.9), (124.8), 78.5, 59.5, 49.9, 47.5, 45.3, (39.6, 38.6, 37.8, 37.3), 28.3, 26.1, 20.2, 18.8, and 13.7; MS *m*/*z* 402 (M^+); Anal. Calcd. for $C_{27}H_{34}OSi$: C, 80.5%; H, 8.5%. Found: C, 80.3.4%; H, 8.5%.

1,1-Bis(*l*-menthoxy)-2,5-diphenylsilacyclopent-3-ene (**6d**): Yield 77% in a reaction at 110 °C for 10 h; ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 7.08–7.25 (m, aromatic H, 10H), 6.24 (s, = CH for trans 2H), 6.17 (s, = CH for cis 2H), 3.26 (s, CH for trans, 2H), 3.13 (s, CH for cis, 2H), 3.79–3.83 (m, OCH, 1H), 3.37–3.42 (m, OCH, 2H), 3.30–3.37 (m, OCH, 2H), 2.84–2.95 (m, OCH, 1H), 2.30–2.39 (m, CH, 1H), 2.02–2.20 (m, CH, 2H), 1.75–1.80 (m, CH, 1H), 0.22–0.17 (m, CH, CH_2, and CH_2, 34H); ^{13}C-NMR δ for each pair of cis and trans isomers: (141.5, 141.3), (135.1, 134.3), (128.4, 128.2), (127.3, 127.2), 124.7, 73.7, (59.4, 59.1, 59.0), 49.9, 45.7, 34.4, 31.6, 25.5, 23.0, 22.6, 21.1, and 16.2; MS *m*/*z* 554 (M^+); Anal. Calcd. for $C_{36}H_{52}O_2Si$: C, 79.3%; H, 9.6%. Found: C, 79.0%; H, 9.8%.

1,1-Bis(*l*-borneoxy)-2,5-diphenylsilacyclopent-3-ene (**6′d**): Yield 76% in a reaction at 110 °C for 10 h; ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 7.10–7.26 (m, aromatic H, 10H), 6.23 (s, = CH for the trans isomer 2H), 6.17 (s, = CH for the cis 2H), 4.25–4.37 (d, OCH J = 6.9 Hz, 1H), 3.88–3.96 (d, OCH J = 6.9 Hz, 2H), 3.40–3.53 (d, OCH J = 6.9 Hz, 1H), 3.26 (s, CH for trans 2H), 3.13 (s, CH for the cis isomer, 2H), 2.28–0.18 (m, CH, CH_2, and CH_2, 34H); ^{13}C-NMR δ for each pair of cis and trans isomers: (141.5, 141.3), (135.1, 134.3), (128.4, 128.2), (127.3, 127.2), 124.7, 78.5, 59.5, 49.9, 47.5, 45.3, 28.3, 26.1, 20.2, 18.8, and 13.7; MS *m*/*z* 540 (M^+); Anal. Calcd. for $C_{36}H_{48}O_2Si$: C, 80.0%; H, 9.0%. Found: C, 79.9%; H, 9.0%.

Table 5. Experimental parameters for X-ray diffraction study of *l*-borneoxy-1-methylsilacyclopentene (**6′c**).

Parameter	**6′c**
Formula	$C_{27}H_{34}OSi$
Molecular weight	402.24
Crystal color	Colorless
Crystal system	Monoclinic system
Space group	$P2_1$
Cell constants	
a, Å	11.585 (7)
b, Å	7.273 (4)
c, Å	14.073 (8)
α, deg	90.00
β, deg	97.605 (11)
γ, deg	90.00
Z	2
Radiation type	Mok/α (λ = 0.71073 Å)
Temperature (°C)	20
No. of data collected	1639
No. of rflns	8833
$R = \Sigma(\lvert F_o - \lvert F_c\rvert)/\Sigma\lvert F_o\rvert$, %)	7.71
$Rw = [\Sigma(\lvert F_o - \lvert F_c\rvert)^2/\Sigma w\lvert F_o\rvert]^{1/2}$, %)	14.9

Table 6. Atomic coordinates and isotropic thermal parameters for the non-hydrogen atoms of *l*-borneoxy-1-methylsilacyclopentene (**6′c**).

Atom	x	y	z	Ueq′[a] Å^2
Si1	0.36143 (13)	0.2793 (3)	0.71459 (11)	0.0416 (5)
O1	0.3318 (3)	0.3490 (5)	0.8185 (2)	0.0481 (12)
C1	0.1647 (5)	0.0787 (10)	0.6116 (4)	0.0452 (17)
C2	0.0554 (6)	0.0715 (12)	0.6429 (5)	0.065 (2)
C3	−0.0083 (7)	−0.0838 (12)	0.6370 (5)	0.072 (2)
C4	0.0319 (7)	−0.2415 (14)	0.5980 (5)	0.075 (3)
C5	0.1382 (7)	−0.2449 (13)	0.5671 (5)	0.073 (2)
C6	0.2055 (6)	−0.0776 (11)	0.5728 (5)	0.065 (2)
C7	0.2372 (5)	0.2493 (10)	0.6170 (4)	0.0536 (19)
C8	0.2975 (5)	0.2878 (11)	0.5314 (4)	0.0601 (18)
C9	0.3952 (6)	0.3875 (10)	0.5468 (4)	0.060 (2)
C10	0.4393 (5)	0.4530 (8)	0.6435 (4)	0.0445 (17)
C11	0.5689 (6)	0.4723 (11)	0.6701 (4)	0.0537 (19)
C12	0.6159 (6)	0.6106 (11)	0.7279 (5)	0.063 (2)
C13	0.7333 (8)	0.6300 (13)	0.7540 (5)	0.087 (3)
C14	0.8073 (7)	0.4916 (18)	0.7270 (6)	0.094 (4)
C15	0.7631 (7)	0.3633 (17)	0.6685 (6)	0.105 (4)
C16	0.6442 (6)	0.3442 (11)	0.6415 (5)	0.067 (2)
C17	0.4454 (6)	0.0632 (11)	0.7386 (5)	0.070 (2)
C18	0.2728 (5)	0.5114 (11)	0.8403 (4)	0.0496 (19)
C19	0.1389 (5)	0.4803 (11)	0.8327 (5)	0.059 (2)
C20	0.1144 (6)	0.5559 (11)	0.9297 (5)	0.064 (2)
C21	0.1525 (6)	0.4053 (12)	1.0022 (5)	0.082 (3)
C22	0.2903 (5)	0.4149 (12)	1.0072 (5)	0.070 (3)
C23	0.3075 (5)	0.5774 (8)	0.9408 (4)	0.0360 (15)
C24	0.2029 (6)	0.7045 (9)	0.9548 (5)	0.0497 (18)
C25	0.1864 (6)	0.8628 (11)	0.8867 (6)	0.087 (3)
C26	0.2095 (6)	0.7794 (14)	1.0558 (5)	0.098 (3)
C27	0.4293 (6)	0.6581 (11)	0.9562 (5)	0.074 (2)

[a] Ueq = $1/3\Sigma i\Sigma j$Uij(ai*·aj*)(ai·aj).

*Isolation of the trans 1,1-disubstituted derivatives of the 2,5-diphenylsilacyclopent-3-enes, **6d′** and **6′d′***
General procedure: Compound **6d** or **6′d** was lithiated by lithium diisopropylamide (LDA) in THF at −78 °C for 8 h, then reacted with acetic acid in THF at −78 °C to afford back **6d** or **6′d**, and the products **6d′** and **6′d′** which were separated from the residue by column chromatography (eluent: hexane).

trans-1,1-Bis(borneoxy)-2,5-diphenylsilacyclopent-3-ene (**6′d′**): Yield 51% in a reaction at −78 °C for 8 h; ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 7.10–7.26 (m, aromatic H, 10H), 6.23 (s, = CH, 2H), 4.25–4.37 (d, OCH J = 6.9 Hz, 1H), 3.88–3.96 (d, OCH J = 6.9 Hz, 2H), 3.40–3.53 (d, OCH J = 6.9 Hz, 1H), 3.26 (s, CH, 2H), 2.28–0.18 (m, CH, CH_2, and CH_2, 34H); ^{13}C-NMR δ: 141.5, 135.1, 128.2, 127.2, 124.7, 78.5, 59.5, 49.9, 47.5, 45.3, 28.3, 26.1, 20.2, 18.8, and 13.7; MS m/z 540 (M^+); Anal. Calcd. for $C_{36}H_{48}O_2Si$: C, 80.0%; H, 9.0%. Found: C, 79.9%; H, 9.0%.

X-ray structure determination

X-ray quality crystals of **6′c** were grown from a concentrated hexane solution of **6′c**. A single crystal of **6′c** was mounted in a thin-walled glass capillary and sealed under nitrogen. Details on machine parameters, crystal data, data collection and refinement are given in Tables 5 and 6.

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